

## Relationship Between Fuel Composition and Properties.

### III - Physical Properties of U. S. Navy Shale-II Fuels

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#### INTRODUCTION

The U. S. Navy has been involved for some time in the development of Navy fuels from alternative sources (shale oil, tar sands and coal) and as a part of this effort, the Naval Research Laboratory and the Naval Air Propulsion Center have been studying the characteristics of these fuels (1,2). NRL and NAPC are currently participating in a program to characterize the products from the Shale-II refining process conducted by the Standard Oil Company of Ohio (SOHIO) at their refinery in Toledo, Ohio. This paper is concerned with a part of this program and is a summary of the work on the physical and related properties of three military type fuels derived from shale: JP-5 and JP-8 jet turbine fuels, and diesel fuel marine (DFM) (3-5). Another paper of this symposium (6) will discuss the chemical characterization of the fuels.

JP-5 (3) is a "high flash point" Navy fuel for carrier-based jet aircraft and helicopters and occasionally for shipboard power plants and propulsion. JP-8 (4), a U. S. Air Force jet fuel, is very similar to "Jet A" kerosene used by commercial jet aircraft in the United States and elsewhere.

The shale derived fuels which were used in these studies were derived from Paraho crude shale oil. The refining process which was used is described elsewhere (7).

A total of thirty-six Shale-II fuel samples have been examined including seventeen JP-5 samples, five JP-8 samples and fourteen DFM samples. Of the thirty-six samples, twenty-six were "finished" fuels in that they had been treated with sulfuric acid to remove organic bases, and ten were "pre-acid treatment" samples. Six of the finished samples did not contain additives but the remaining twenty samples did. The latter group included two pilot plant samples, one JP-5 ("J-PP") and one DFM ("D-PP").

#### GC SIMULATED DISTILLATION

The boiling range distribution of a representative sample of each of the three fuels was determined by gas chromatography (GC Simulated Distillation) using ASTM method D 2887 (8). Data are given in Table I and plots of the data for JP-5 and DFM are shown in Figure 1. JP-8 data have been omitted from the figure since the data for JP-5 and JP-8 are quite similar. The temperatures for the JP-8 averaged 4°C lower than for the JP-5 at the various percentages. The only exception was the 0.5% distilled point, for which JP-5 was

5°C lower. The JP-5 data are somewhat low compared to current JP-5 from petroleum (9). As a rule, data obtained by a GC simulated distillation do not agree with analogous data obtained by actual distillation. Temperatures by the simulated distillation are lower than that of simple ASTM pot distillations (10) at the initial temperatures, higher near the end point temperatures, and in close agreement near the midpoint temperatures (3,4). From the distillation data and other data which follow, the JP-8 Shale-II samples can be considered to be "JP-5" fuel for all practical purposes.

#### MISCELLANEOUS PHYSICAL PROPERTIES

Specific gravity, freezing point and pour point data are shown in Table II. For each fuel four kinds of data are given (where available): the range of the data (minimum and maximum values obtained), the average value for all the samples examined, the military specification requirement for that property, and an average value for a representative petroleum derived fuel. Also shown in the table are the number of fuel samples which were examined in each case. This format is also used for Table III which will follow.

Specific Gravity - The specific gravities of the Shale-II jet fuels (one sample of each type) were very similar to each other, met specification requirements, and were about the same as that of an average petroleum derived fuel. The two Shale-II DFM specific gravities were very similar but slightly lower than that of an average petroleum derived fuel.

Freezing Point - With the exception of one JP-8 sample (J-11), all the samples of the jet fuels froze below the specification maximum. The single exception froze less than 0.5°C above the allowed value for JP-8, -50°C. The similar freezing points for the JP-5 and JP-8 samples reinforce the conclusion from the distillation data that the two types of jet fuels made in the SOHIO process are very similar. The highest JP-5 freezing point was that of the pre-acid treatment sample (J-7) which froze at -46.8°C. The freezing point of jet fuels is greatly affected by the concentration of the higher n-alkanes, such as n-hexadecane (1). The relationship between freezing point and the concentration of n-hexadecane in the fuel appears to be consistent with that of the Shale-I studies. The amount of these alkanes in the Shale-II jet fuels is relatively low (6), a result of keeping the distillation end point lower than normal (3,4).

Pour Point - The pour points of each of two samples of DFM were -20.6°C. This value is well below the specification maximum of -6.7°C (4) and that of an average petroleum derived DFM (11,12).

#### FLAMMABILITY, IGNITION AND ELECTROSTATIC PROPERTIES

Flammability, ignition, and electrostatic properties are shown in Table III. As in the case of the miscellaneous physical properties (Table II), the range of the data, averages, specification requirements, and representative values for petroleum derived fuels are given in the table.

Flash Point - Flash points were determined by the Tag closed cup method (16) rather than by the Pensky-Martens method (20) as

called for in the specifications for JP-5 (3) and DFM (5). The Tag closed cup, however, is specified for JP-8 (4). The Tag method was chosen in order to have a basis of comparison for all three fuels and because it gives values which are closer to the lower flammability temperature limits which is important from the standpoint of safety. For fuels in the JP-5/DFM flash point range, the Tag method gives values which are 2-4°C lower than that of the Pensky-Martens (12). The JP-8 and the DFM flash points are seen to be well above the specification requirements of 38° and 60°C (4,5). In the case of the JP-5 samples, four of the six samples had Tag flash points which were below the required 60°C (3). However, if we assume that the Pensky-Martens flash points would average about 3°C higher, four of the six samples would then meet the 60°C minimum and the other two would be less than a degree low. The Shale-II JP-8 flash point data are somewhat higher than that of an average petroleum derived JP-8 and quite close to that of the Shale-II JP-5.

Autoignition Temperatures - The autoignition data (AIT) shown in Table III were determined by ASTM D 2155 (17). The Shale-II JP-8 and DFM AIT values (238°C) were identical and similar to that of their petroleum derived counterparts. The Shale-II JP-5 AIT (232°C), however, was slightly lower than that of the other two fuels as well as that of representative petroleum JP-5 (241°C), but was well within the 11°C reproducibility limit set by the method (17). There are no AIT requirements in the military specifications for JP-5, JP-8 and DFM (3-5).

Electrostatic Properties - Electrostatic data are shown in Table II. The electrical conductivity and charging tendency of jet fuels are important with respect to electrical charge buildup in flowing fuel equipment, particularly filter separators. Electrical charge buildup can result in a spark discharge capable of igniting flammable vapors if they are present. This is a frequent cause of accidental fires and explosions and is an important factor in safety. Therefore, these properties were measured on the Shale-II jet fuels to determine if these fuels posed a lesser or greater hazard than their petroleum-derived counterparts. The values which were found for the Shale-II jet fuels in Table III are in the normal ranges found for petroleum derived jet fuels. The response to the addition of a static dissipator additive, ASA-3, is also normal. These Shale-II jet fuels behaved significantly different than the Shale-I JP-5 which exhibited abnormally high electrical conductivity (215 pS/m) and charging tendency (7035  $\mu\text{C}/\text{m}$ ) without the addition of any additives (2).

#### COPPER CORROSION

Tests for corrosion are of a qualitative type and are made to determine whether the fuel is free of tendency to corrode copper bearing alloys in aircraft pumps. The results of the ASTM copper strip corrosion tests (22) are shown in Table IV. The samples in the table are grouped in accordance with their refining treatment and by the additives the fuels were reported to contain. The fuels fall into four groups as seen in Table IV: (a) nine samples taken in the refining process before the acid treatment; (b) six finished samples which contained no additives; (c) nine jet fuels containing fuel system icing inhibitor (FSII) and an anti-oxidant; and (d) finished fuels

containing only anti-oxidant. In the table a "+" or "-" sign is used in each column to show the applicability of the column headings. In the case of the FSII column, seven of the nine jet fuels which contained the icing inhibitor show actual data in place of the "+" symbol. In those cases, concentration was determined by analysis (23). The specification requirement (3,4) for both jet fuels is 0.10 - 0.15% FSII (ethylene glycol monomethyl ether).

The corrosion test results are shown in the last column. In order to meet the specification requirement (3,4), a maximum value of "1" is acceptable in a scale of one through four (22). For example, "1B" would pass, but "2A" would not. It is seen in the table that only one of the nine pre-acid treatment samples and one of the six additive free finished samples failed the test. But of the sixteen additive containing samples, only two (J-PP and D-PP) passed the test. These two samples were pilot plant samples which contained a different anti-oxidant, AO-29. Since almost all of the finished samples failed the test and since most of the pre-acid or non-additive samples passed the test, these results need to be related to the sequence of operations in the refinery process and to the nature of the additives which were used. It seems probable that either there was a problem with the acid treatment process by which a corrosive species was produced which ended up in the finished samples or that the additives used may have been contaminated. Both aspects may be involved.

Free sulfur (17 ppm) and mercaptans (10 ppm) have been detected in the Shale-II JP-5. Model studies found that the combined presence of these two species, each at about the 10 ppm level, can cause failure of the copper corrosion test. The anti-oxidant, AO-30, exhibited indications of reinforcing the effects of the sulfur species in the model studies. Fortunately, a concentration of 5 ppm of benzotriazole enables Shale-II JP-5 to pass the copper strip corrosion test.

#### CONCLUSIONS

The physical properties of the Shale-II fuels were similar to that of equivalent fuels derived from petroleum. The differences observed could be minimized by modest changes in refining steps.

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#### REFERENCES

- (1) J. Solash, R. N. Hazlett, J. M. Hall, C. J. Nowack, *Fuel*, 57, 521 (1978).

- (2) W. A. Affens, J. T. Leonard, G. W. McLaren and R. N. Hazlett, Preprints, Symposium on Oil Shale, Tar Sands, and Related Materials, Division of Fuel Chemistry, Amer. Chem. Soc., 21, No. 6, 249 (Sept. 1976).
- (3) Military Specification, Turbine Fuel, Aviation Grades, JP-4 and JP-5, MIL-T-5624L, 18 May 1979.
- (4) Military Specification, Turbine Fuel, Aviation, Kerosene Type, Grade JP-8, MIL-T-83133A, 18 May 1979.
- (5) Military Specification, Fuel Oil, Diesel Marine, MIL-F-16884G, 7 March 1973; Amend. 22 March 1978.
- (6) J. Solash, R. N. Hazlett, J. C. Burnett, E. Beal, and J. M. Hall, "Relation Between Fuel Properties and Chemical Composition. II. Chemical Characterization of U. S. Navy Shale-II Fuels", This Symposium.
- (7) L. W. Kruse and E. T. Robinson, "Shale Oil- II Pilot Plant Refining Studies", Naval Air Systems Command-Naval Research Laboratory Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels," 37-57, June 15-16, 1978.
- (8) "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography", Amer. Soc. for Test. and Mater., ASTM D2887, 1973.
- (9) E. M. Shelton, "Aviation Turbine Fuels, 1978," Bur. of Mines, Petrol. Survey 109, May 1979.
- (10) "Distillation of Petroleum Products," Amer. Soc. for Test. and Mater., ASTM D86 (1972).
- (11) "Distillate Fuel Economic Study," Nav. Ship Engr. Center, May 1974.
- (12) W. A. Affens, "Shipboard Safety - A Meaningful Flash Point Requirement for Navy Fuels," Naval Research Laboratory Report 7999, Oct. 28, 1976.
- (13) "Density and Relative Density (Specific Gravity) of Liquids by Bingham Pycnometer," Amer. Soc. for Test. and Mater., ASTM D1217 (1976).
- (14) "Freezing Point of Aviation Fuels," Amer. Soc. for Test. and Mater., ASTM D2386 (1972).
- (15) "Pour Point of Petroleum Oils," Amer. Soc. for Test. and Mater., ASTM D97 (1971).
- (16) "Flash Point by Tag Closed Tester," Amer. Soc. for Test and Mater., ASTM D56 (1975).
- (17) "Autoignition Temperature of Liquid Petroleum Products," Amer. Soc. for Test. and Mater., ASTM D2155 (1976).

- (18) "D-C Electrical Conductivity of Hydrocarbon Fuels," Amer. Soc. for Test. and Mater., ASTM D3114 (1972).
- (19) D. A. Young, "Mini-Static Test Procedure", Exxon Research and Engineering Co., Linden, N. J., June 1972.
- (20) "Flash Point by Pensky-Martens Closed Tester," Amer. Soc. for Test. and Mater., ASTM D93 (1974).
- (21) Coordinating Research Council, "A Survey of Electrical Conductivity and Charging Tendency Characteristics of Aircraft Turbine Fuels," CRC Report 478, April 1975.
- (22) "Detection of Copper Corrosion from Petroleum Products by the Copper Strip Tarnish Test," Amer. Soc. for Test. and Mater., D130 (1976).
- (23) "Fuel System Icing Inhibitor in Hydrocarbon Fuels (Iodometric Method)," Fed. Test Method Std. 791B, Method 5327.3, Jan. 15, 1969.

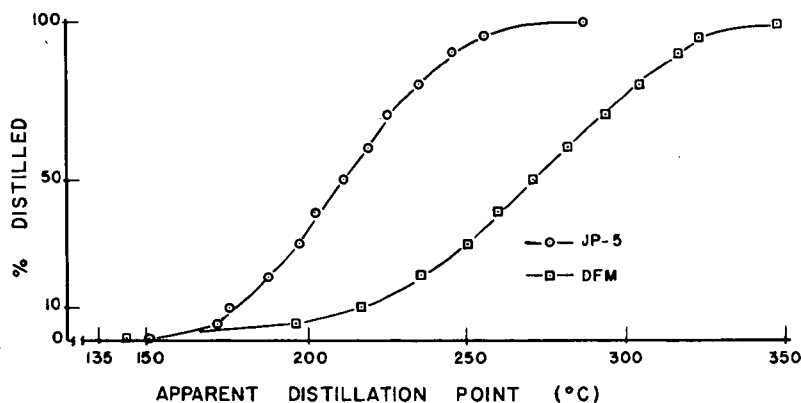


FIGURE 1 - GC SIMULATED DISTILLATION OF SHALE-II FUELS

TABLE I. GC Simulated Distillation\*

<u>Percent Distilled</u>	<u>Temperature (°C)</u>		
	<u>JP-8 (J-11)</u>	<u>JP-5 (J-18)</u>	<u>DFM (D-1)</u>
0.5	156	151	144
5.0	169	172	196
10.0	175	177	217
20.0	182	187	235
30.0	191	197	250
40.0	199	202	260
50.0	205	211	271
60.0	216	219	282
70.0	221	224	294
80.0	231	234	305
90.0	240	245	316
95.0	253	255	323
99.5	281	287	347

\*ASTM D2887 (8)

TABLE II. Miscellaneous Physical Properties

	<u>Specif. Grav. (25/25°C)<sup>a</sup></u>	<u>Freezing Point<sup>b</sup> (°C)</u>	<u>Pour Point<sup>c</sup> (°C)</u>
<u>JP-5 (10 samples)</u>			
Range	-	-46.8 - -51.7	-
Average	0.8122 <sup>d</sup>	-49.7	-
Specification	0.788 - 0.845	-46 (max.)	-
Petroleum <sup>e</sup>	0.818	-49	-
<u>JP-8 (2 samples)</u>			
Range	-	-49.6 - -50.4	-
Average	0.8098 <sup>d</sup>	-50.0	-
Specification	0.775 - 0.830	-50 (max.)	-
Petroleum <sup>e</sup>	0.810	-54	-
<u>DFM (2 samples)</u>			
Range	0.8390 - 0.8393	-	-20.6 <sup>f</sup>
Average	0.8392	-	-20.6
Specification	-	-	-6.7 (max.)
Petroleum <sup>e</sup>	0.850	-	-14

a - ASTM D 1217 (13)

b - ASTM D 2386 (14)

c - ASTM D 97 (15)

d - One sample tested.

e - Data for representative petroleum derived fuel (9,11,12)

f - Same result for both samples.

TABLE III. Flammability, Ignition and Electrostatic Properties

	Flash Point (°C) <sup>a</sup>	AIT (°C) <sup>b</sup>	Conductivity (pS/m) <sup>c</sup>	Charging Tendency ( $\mu\text{C}/\text{m}$ ) <sup>d</sup>
<u>JP-5 (6 samples)</u>				
Range	55.1 - 61.2			
Average	58.0	232 <sup>e</sup>	6.6 <sup>e</sup> (228) <sup>f</sup>	2100 <sup>e</sup> (16600) <sup>f</sup>
Specification	60 (min.) <sup>g</sup>			
Petroleum	64	241	0.8 - 15	1500 - 4000
<u>JP-8 (2 samples)</u>				
Range	53.4 - 58.7			
Average	56.1	238 <sup>e</sup>	5.3 <sup>e</sup> (142) <sup>f</sup>	890 <sup>e</sup> (12300) <sup>f</sup>
Specification	38 (min.)		200 (min.) - 600 (max.)	
Petroleum	53	238		
<u>DFM (2 samples)</u>				
Range	71-75	238 <sup>e</sup>		
Average	73.4	238 <sup>e</sup>		
Specification	60 (min.) <sup>g</sup>			
Petroleum	79	240		
a - ASTM D 56 (16) b - ASTM D 2155 (17) c - ASTM D 3114 (18) d - Exxon Minitester (19) (Measured with Type 10 filter paper) e - One sample tested f - One ppm ASA-3 added; result with additive in parenthesis g - ASTM D 93 (20) h - Data for representative petroleum derived fuel (9, 11, 12, 21)				



TABLE IV. Copper Strip Corrosion Tests

<u>Sample</u>	<u>Fuel</u>	<u>Pre-Acid Treat.</u>	<u>Acid Treated Fuel None</u>	<u>Sample Additives<sup>g</sup> FSII (%v/v)<sup>a</sup> Anti-Oxid.<sup>b</sup></u>	<u>Test Result<sup>c</sup></u>
J-7	JP-5	+	-	-	1A
J-8	"	+	-	-	1A
J-9	"	+	-	-	1A
J-10	"	+	-	-	1A
J-13	JP-8	+	-	-	3B
J-14	"	+	-	-	1A
D-7	DFM	+	-	-	1A
D-8	"	+	-	-	1A
D-10	"	+	-	-	1B
J-1	JP-5	-	+	0 <sup>d</sup>	1A
J-19	"	-	+	0 <sup>d</sup>	1A
J-11	JP-8	-	+	0 <sup>d</sup>	1A
J-12	"	-	+	0 <sup>d</sup>	1A
J-17	"	-	+	0 <sup>d</sup>	1A
D-1	DFM	-	+	-	2C
J-PP	JP-5	-	-	0.11 <sup>d</sup>	1A
J-2	"	-	-	0.21 <sup>d</sup>	3B
J-3	"	-	-	+ <sup>e</sup>	3B
J-4	"	-	-	0.20 <sup>d</sup>	3B
J-5	"	-	-	+ <sup>e</sup>	3B
J-6	"	-	-	0.19 <sup>d</sup>	3B
J-16	"	-	-	0.18 <sup>d</sup>	3B
J-18	"	-	-	0.09 <sup>d</sup>	3B
J-22	"	-	-	0.10 <sup>d</sup>	3B
D-PP	DFM	-	-	+ <sup>f</sup>	1A
D-2	"	-	-	+	3B
D-3	"	-	-	+	3B
D-5	"	-	-	+	3B
D-6	"	-	-	+	3B
D-11	"	-	-	+	3B
D-12	"	-	-	+	3B

a - Ethylene glycol monomethyl ether fuel system icing inhibitor (3, 4)

b - Anti-oxidant "AO-30" (2,4-dimethyl-6-tertiary-butyl phenol).

c - ASTM D 130 (22). Specification (max.) = 1B (3-5)

d - By FSII determination (23)

e - FSII reported to be present (0.10 - 0.15%) (3,4)

f - Anti-oxidant "AO-29" (2,6-ditertiary-butyl-4-methyl-phenol) in pilot plant fuels.